RESULTS FROM FOOD MONITORING PROGRAM FOR DIOXINS IN COMUNITAT VALENCIANA (SPAIN): 2004-2005

Montaña MJ[1], Bescós L[1], Martí R[1], Ferrer C[2], Yusà V[2], Díaz-Ferrero J[1]

[1]Environmental Laboratory, Institut Químic de Sarrià (Ramon Llull University), Via Augusta 390, 08017 Barcelona (Spain), e-mail: jordi.diaz@iqs.edu; [2] Direcció General de Salut Pública, Conselleria de Sanitat (Generalitat Valenciana), Micer Mascó 31-33, 46010 València (Spain).

INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) are two families of compounds that accumulate in animals and humans due to their properties of persistence and high lipophilia. PCDD/Fs are not intentionally produced, but they are formed as by-products of chemical or thermal processes. However, their bioaccumulation and biomagnification through the food chain make food the main exposition of human to these compounds (higher than 90 %)[1]. Based on this fact, EU have established maximum values of PCDD/F in foodstuffs[2-3]. It have also recommended to set monitoring programmes to control PCDD/F levels, with a number of samples per country to be analyzed[4]. In this paper, results from the monitoring program in Comunitat Valenciana corresponding to year 2004 and 2005 are presented.

METHODS AND MATERIALS

Samples analysed

Samples were collected by the local Public Health Centres in Comunitat Valenciana (Spain). Table 1 shows the number of each food category collected in year 2004 and year 2005.

Table 1. Samples analysed

Category	Year 2004	Year 2005
Meat	13 (6 ruminants, 4 poultry, 3 pork)	14 (6 ruminants, 4 poultry, 4 pork)
Fish and seafood	14	14
Eggs	9	7
Milk and dairy products	4	4
Vegetable oils	3	3
Animal fat	2	2
Cereals	0	4
Vegetables	0	7
Fruit	0	5
Total	45	60

Analytical method

Determination of PCDD/F were performed following analytical methods based on international norms for dioxin analysis (USEPA 1613[5]) and European Directives related to this subject[6]. The specific methodology depends on which foodstuff is being analysed, especially the extraction step. However, the following scheme of analysis is shared by all the methods:

1) Homogenisation of the sample to assure that the sub-sample taken for the analysis represents the whole foodstuff.
2) Sample weighing. The weight usually depends on the fat contents of the foodstuff.
3) Addition of extraction internal standards labelled with ^{13}C to the sample.
4) Extraction of the fat fraction (including the compounds of interest). Extraction methodology depends on the type of sample: liquid-liquid extraction, solid-liquid extraction in Soxhlet, etc. have been used.

5) Clean-up of fat extract and fractionation of PCDD/F and PCB. These steps are usually performed by liquid chromatography on different adsorbents: silica, silica modified with several reagents (sulphuric acid, sodium hydroxide, etc.), Florisil, graphitized carbon, etc.
6) Concentration of the purified extract and addition of syringe standards.
7) Instrumental analysis: It is carried out by HRGC-HRMS.
8) Quantitation: Samples are quantitated by the isotopic dilution method.

RESULTS AND DISCUSSION

PCDD/F concentration

The levels of PCDD/F detected in the samples are shown in Table 2 and Table 3. Mean and median concentrations in WHO-TEQ (upperbound[6]), as well as maximum and minimum values, are presented.

Table 2. PCDD/F concentration in 2004 samples.

Category	Units	n	Mean	Median	Min	Max
Meat-ruminants	pg TEQ/g l.w.	6	0.51	0.53	0.33	0.59
Meat-poultry	pg TEQ/g l.w.	4	0.83	0.87	0.39	1.19
Meat-pork	pg TEQ/g l.w.	3	0.74	0.17	0.15	1.91
Fish and seafood	pg TEQ/g f.w.	14	0.16	0.11	0.02	0.62
Eggs	pg TEQ/g l.w.	9	0.96	0.90	0.44	1.65
Milk and dairy products	pg TEQ/g l.w.	4	0.84	0.85	0.46	1.18
Vegetable oils	pg TEQ/g l.w.	3	0.10	0.09	0.09	0.13
Animal fat	pg TEQ/g l.w.	2	0.17	0.17	0.13	0.21

Table 3. PCDD/F concentration in 2005 samples.

Category	Units	n	Mean	Median	Min	Max
Meat-ruminants	pg TEQ/g l.w.	6	0.57	0.45	0.26	1.18
Meat-poultry	pg TEQ/g l.w.	4	0.85	0.83	0.51	1.23
Meat-pork	pg TEQ/g l.w.	4	0.26	0.24	0.12	0.44
Fish and seafood	pg TEQ/g f.w.	14	0.19	0.16	0.05	0.55
Eggs	pg TEQ/g l.w.	7	0.43	0.39	0.34	0.62
Milk and dairy products	pg TEQ/g l.w.	4	0.75	0.68	0.66	0.92
Vegetable oils	pg TEQ/g l.w.	3	0.17	0.16	0.14	0.20
Animal fat	pg TEQ/g l.w.	2	0.14	0.14	0.13	0.14
Cereals	pg TEQ/g f.w.	4	0.05	0.04	0.04	0.06
Vegetables	pg TEQ/g f.w.	7	0.08	0.08	0.05	0.09
Fruit	pg TEQ/g f.w.	5	0.07	0.06	0.04	0.12

Most of the 105 samples analysed were below the maximum levels established by European regulations. Only one pork meat sample was above 1 pg TEQ/g l.w., which is the level set for this kind of meat.

In general, concentrations in TEQ were quite similar for samples collected during 2004 and 2005. The most important differences were found in egg samples, where the range of PCDD/F level was wider and higher in 2004 (0.44-1.65 pg WHO-TEQ/g lipid weight) than in 2005 (0.34-.62 pg WHO-TEQ/g lipid weight). Detected values in the different categories of foodstuffs were in the same order as those reported by other authors for different Spanish areas[7-10].

Profiles

The profile of the 2,3,7,8-chlorosubstituted congeners was studied for each sample and a typical profile was obtained for each category (Figure 1). Most of these profiles were characterised by higher concentrations of OCDD. Only fish samples show a different trend, with low chlorination furans (especially, 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF) at the highest levels. In milk and dairy products, the contribution of 2,3,4,7,8-PeCDF to the profile is also important.

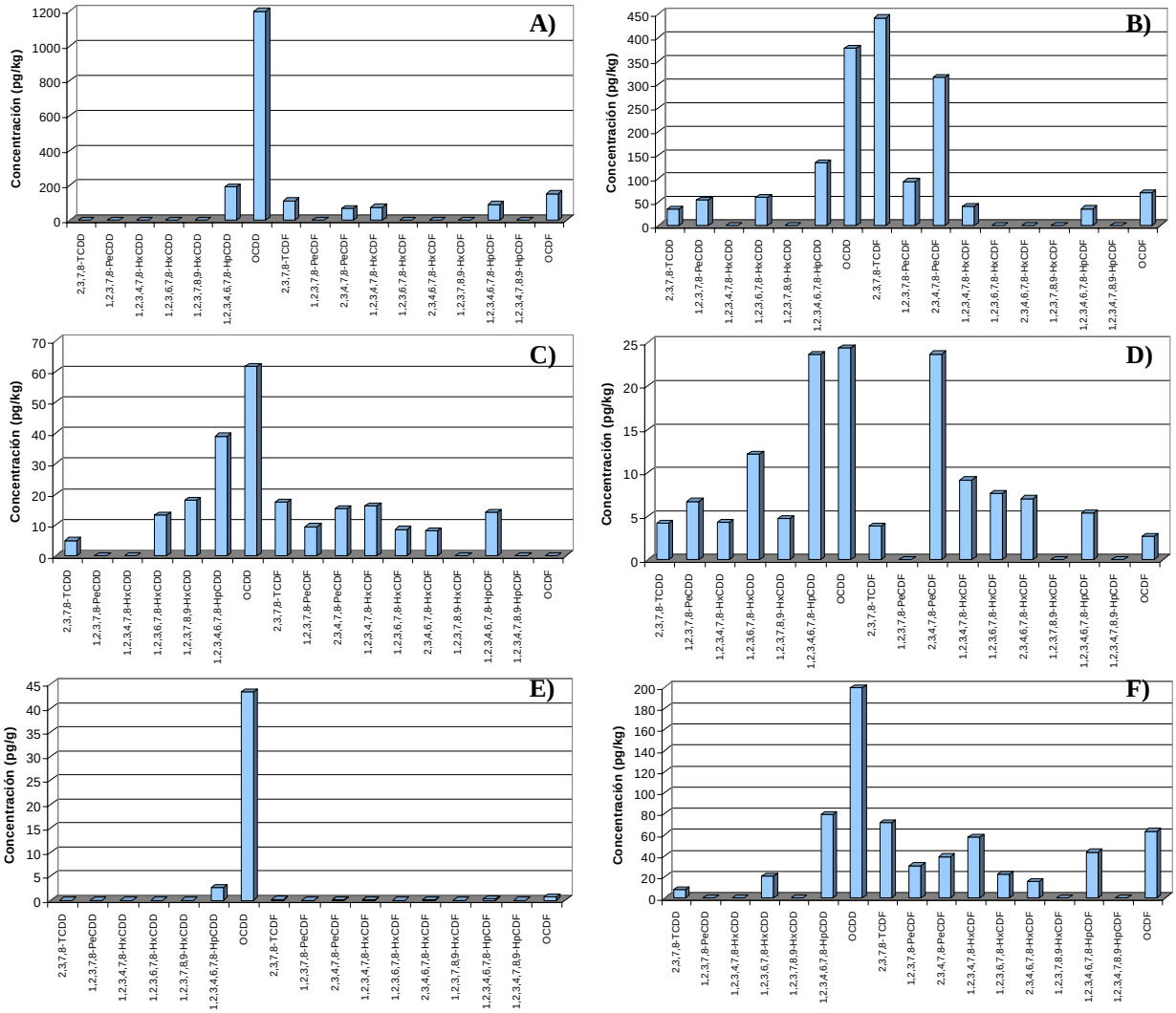

Figure 1. *Characteristic profiles obtained in the different categories of studied foodstuffs: (a) Meat, (b) Fish, (c) Eggs, (d) Milk and dairy products, (e) Oil and fats, (f) Vegetables.*

Evaluation of daily intake

Based on the results obtained from the PCDD/F analyses (median of each category expressed in pg WHO-TEQ/g fresh weight) in 2004-2005 and on the food consumption in Comunitat Valenciana (g/day)[12], the PCDD/F daily intake was estimated. The result was 0.91 pg TEQ/kg b.w./day. This value is coherent with those reported for different areas of Spain in other studies[7-11] and it is close to the lower limit of the range established by WHO in the last reevaluation of the tolerable daily intake of PCDD/F[12] (1-4 pg TEQ/kg b.w./day).

Figure 2 shows the contribution of each category to the total intake. Groups from animal origin contribute 50% of the total intake. However, vegetables and fruits make also an important contribution due to the high consumption in the Mediterranean diet.

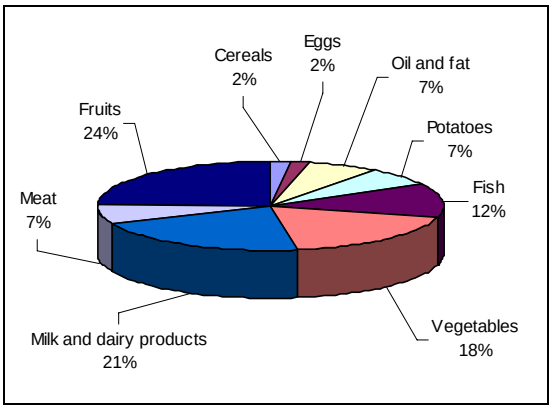

Figure 2. *Contribution of each food category to the total PCDD/F daily intake in Comunitat Valenciana.*

REFERENCES

1. Galli CL, Marinovich M; *Organohalogen Compounds* 1999; 44:427.
2. Council Regulation 2375/2001 of 29 November 2001, Official Journal of the European Communities L321/1.
3. Comission Regulation 199/2006 of 3 February 2006. Official Journal of the European Communities L32/34.
4. Comission Recommendation 2004/705/EC of 11 October 2004. Official Journal of the European Communities L321/45.
5. EPA 1613 Method: Tetra-Through Octa Chlorinated Dioxins and Furans by Isotope Dilution HRGC-HRMS Revision B (1994)
6. Comission Directive 2002/69/CE of 26 July 2002, Official Journal of the European Communities L209/5.
7. Fernández MA, Gómara B, Bordajandi LR, Herrero L, Abad E, Abalos M, Rivera J, González MJ; *Food Additives and Contaminants* 2004; 21:983.
8. Bocio A, Domingo JL; *Environmental Research* 2005; 97:1.
9. Llobet JM, Domingo JL, Bocio A, Casas C, Teixidó A, Müller L; *Chemosphere* 2003; 50:1193.
10. Bascompta O, Montaña MJ, Marti R, Broto-Puig F, Comellas L, Díaz-Ferrero J, Rodríguez-Larena MC; *Organohalogen Compounds* 2002; 57:149.
11. Ministry of Agriculture, Fishery and Food. Consumption data 2005. Published at www.mapa.es (15/05/06).
12. World Health Organisation, Assessment of the health risk of dioxins: Re-evaluation of the Tolerable Daily Intake (TDI), 1999.